



Short communication

Study of sulfonated polyether ether ketone with pendant lithiated fluorinated sulfonic groups as ion conductive binder in lithium-ion batteries



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H I G H L I G H T S

- SPEEK-FSA-Li binder is beneficial to the decrease of polarization resistance.
- SPEEK-FSA-Li binder improves charge–discharge plateau potential and capacity.
- SPEEK-FSA-Li binder shows excellent adhesion strength.

A R T I C L E I N F O

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In an attempt to reduce the Li^+ concentration polarization and electrolyte depletion from the electrode porous space, sulfonated polyether ether ketone with pendant lithiated fluorinated sulfonic groups (SPEEK-FSA-Li) is prepared and attempted as ionic conductivity binder. Sulfonated aromatic poly(ether ether ketone) exhibits strong adhesion and chemical stability, and lithiated fluorinated sulfonic side chains help to enhance the ionic conductivity and Li^+ ion diffusion due to the charge delocalization over the sulfonic chain. The performances are evaluated by cyclic voltammetry, electrochemical impedance spectroscopy, charge–discharge cycle testing, 180° peel testing, and compared with the cathode prepared with polyvinylidene fluoride binder. The electrode prepared with SPEEK-FSA-Li binder forms the relatively smaller resistances of both the SEI and the charge transfer of lithium ion transport. This is beneficial to lithium ion intercalation and de-intercalation of the cathode during discharging–charging, therefore the cell prepared with SPEEK-FSA-Li shows lower charge plateau potential and higher discharge plateau potential. Compared with PVDF, the electrode with ionic binder shows smaller decrease in capacity with the increasing of cycle rate. Meanwhile, adhesion strength of electrode prepared with SPEEK-FSA-Li is more than five times greater than that with PVDF.

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1. Introduction

Lithium-ion batteries (LIBs) have attracted considerable attention in the areas of hybrid and completely electric vehicles as well as portable devices due to their high intrinsic energy density and high voltage [1–4]. Typical lithium-ion battery electrodes are composite mixtures obtained by blending electro-active material particles and conductive additives with polymeric binder. Nonionic polymers such as poly(vinylidene difluoride) (PVDF) binder are the most commonly used cathode binder for LIBs. This is ascribed to its good electrochemical stability and adhesive strength, and ability to

absorb electrolyte for transport of Li^+ into/out of the oxide surface [5–8].

Modeling studies suggest that salt concentration polarization and electrolyte loss from the accessible pores in the electrodes are important factors limiting the charge–discharge performance of lithium-ion batteries [9]. Therefore, some efforts have been focused on improving the electronic conductivity of electrodes, such as doping metals into the crystalline lattice of active material [10,11] or adding electronic conductive polymers [12]. Reversible charge and discharge were demonstrated, but satisfactory improvements have not been reported. Maybe the cathodical polarization is related to not only the electronic conductivity of the electrode, but also the lithium ion transportation kinetics of the cathode [13].

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Recently, the use of lithiated ionomers as binders might offer a route to enhance the ionic conductivity and Li^+ ion diffusion by providing ionic functionality within the electrodes. The battery performance is intimately linked with lithium-ion transfer at the interface between the electrode and the electrolyte, as well as in the porous space of the electrode. The lithiated perfluorinated sulfonic ion-exchange material has relatively high ionic conductivity ($\sim 10^{-4} \text{ S cm}^{-1}$) [14–17]. By coprecipitating cathode material with Nafion, the charge–discharge cycling stability was improved at large current density [18,19]. LiFePO_4 cathode prepared with lithiated perfluorosulfonate ionomer as binder was displayed high performance by providing ionic functionality [20]. The ionomer could compensate for and/or prevent the electrolyte depletion from the electrode porous space during discharging.

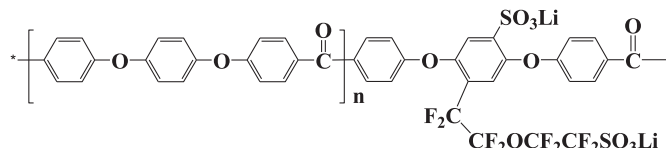
However, these attempts of the early work on ionic conductivity binder have no evaluation of adhesion strength. And the binder content is higher than practical application to enhance the energy density (20 wt% in Ref. [16]). From a practical perspective, adhesion strength is more important than almost any other electrode performance (e.g., cycle life, capacity), since electrochemical property cannot be stable if the adhesion strength is insufficient to bear repeated charging and discharging cycling [21]. Moreover, the cost of perfluorinated ionomer is still a concern in the battery industry.

Aiming to improve the adhesive strength as well as reduce the cathodical polarization, sulfonated polyether ether ketone with pendant lithiated fluorinated sulfonic groups (SPEEK-FSA-Li) was prepared and attempted as ionic conductivity binder. Sulfonated aromatic poly(ether ether ketone) shows good thermal and mechanical stability, and lithiated fluorinated sulfonic side chains have low lithium dissociation energy. The performance of the electrode prepared with SPEEK-FSA-Li binder has been investigated by cyclic voltammetry, electrochemical impedance spectroscopy, charge–discharge testing and 180° peel testing (Scheme 1).

2. Experimental

2.1. Preparation of binder solutions and cathodes

SPEEK-FSA-Li (synthesis and characterization in [Supplementary information](#)), was dissolved at 60°C in 1-methyl-2-pyrrolidone (NMP, AR, Aladdin, China) for 24 h to form a 5 wt% solution. 80 wt% LiFePO_4 (Li Tong Energy Technology Co., Ltd., China) was grinded with 10 wt% Super P (Timcal Graphite & Carbon, Switzerland) before being added into the binder solution. The slurry was then coated on an aluminum foil and dried under the vacuum at 80°C for 24 h. For comparison, a cathode prepared with PVDF (HSV900, Arkema Co., Ltd, France) binder using the similar procedure was prepared under the same conditions, and the mass ratio of LiFePO_4 /Super P/PVDF is also 8/1/1, the same as the LiFePO_4 cathode with SPEEK-FSA-Li. The dried electrodes were compressed by a roller at room temperature to form a smooth and compact film structure. Both electrodes were cut into the shape with an area of 1.32 cm^2 for coin cell use and had a load of about 3.4 mg cm^{-2} LiFePO_4 . Before use, the electrodes were dried for 12 h at 100°C under the vacuum.



Scheme 1. The structural formula of SPEEK-FSA-Li.

2.2. Electrochemical characterization

The electrochemical performances of LiFePO_4 cathodes were evaluated in a 2032 coin-type $\text{LiFePO}_4/\text{Li}$ half-cell, in which the electrolyte was a solution of 1 M LiPF_6 dissolved in a 1:1:1 (volume ratio) mixture of EC/DMC/EMC (Shanghai Shanshan Co., Ltd, China). All the cells were assembled in an argon-filled glove box (Etelux).

Batteries were cycled using a Land CT2001A battery tester at rates of 0.1–2 C between 2.7 V and 4.2 V. After battery formation, the cyclic voltammetry were carried out using a Zahner Zennium EL101 electrochemical station at a rate of 0.2 mV s^{-1} between 2.5 V and 4.5 V. And the impedance spectroscopy measurements were performed over a frequency range of 10^{-2} Hz – 10^6 Hz with potential amplitude of 10 mV.

2.3. Adhesion characterization

The adhesion strength between the coating of electrode materials and the Al current collector was measured by a 180° peeling test using an omnipotent electronic stress–strain tester (UTM, Instron 5567, USA). In the tests, the electrodes were cut to a coated strip of 9 mm width and fixed to a stainless plate with double faced adhesive tape. The stainless plate and Al foil were fixed in upper and lower chuck, respectively. The strip was pulled at a speed of 1.0 cm min^{-1} .

3. Results and discussion

3.1. Cyclic voltammogram (CV)

For practical battery applications, it is important to investigate the electrochemical stability of the binder within the operation voltage of the battery system. The electrochemical stability of the SPEEK-FSA-Li binder was investigated using cyclic voltammetry (CV) as shown in Fig. 1. It can be seen that cathode electrode are stable up to at least 4.5 V versus Li^+/Li . The CV curve of electrode prepared with SPEEK-FSA-Li binder shows the oxidation current peaks for lithium ion de-intercalation during the forward potential scanning and the reduction current peaks for lithium ion intercalation during the backward potential scanning. Therefore, the good electrochemical stability makes it possible to consider the use of binder for cathode materials. In addition, the electrode with SPEEK-FSA-Li binder shows a smaller voltage difference between the oxidation and reduction peak potential than that of the electrode

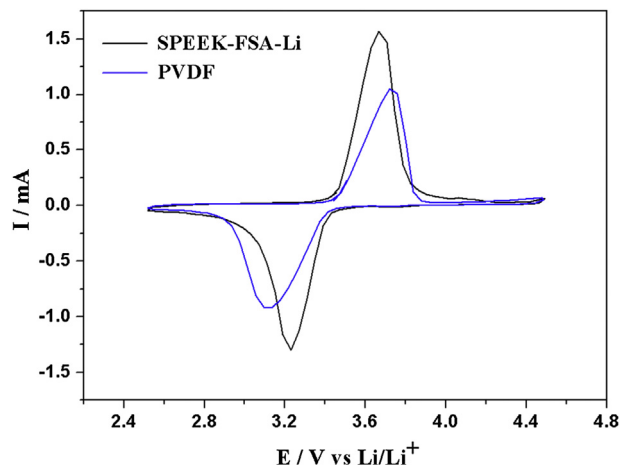


Fig. 1. Cyclic voltammograms of LiFePO_4 electrodes prepared with SPEEK-FSA-Li or PVDF binder.

with PVDF binder, indicated that the electrode with SPEEK-FSA-Li binder has lower polarization.

3.2. Electrochemical impedance spectroscopy (EIS)

Fig. 2 shows the effect of binder type on the experimental electrochemical impedance spectra of LiFePO_4 electrodes. Typically, the impedance spectra of lithium-ion intercalation and de-intercalation in a cathode of lithium ion battery shows three characteristic time constants, corresponding to the high, medium and low frequency range of impedance spectra, respectively. The Nyquist plot shows a large semicircle from the high to medium frequencies and a nearly straight line at low frequencies. The semicircle at high to medium frequencies is generally accepted as the migration of lithium ion in the surface layers, while the low-frequency straight line is likely the result of lithium ions diffusion through the electrodes [22]. By comparing the semicircle size in the medium frequency region, it is clear that the electrode prepared with SPEEK-FSA-Li binder has lower charge transfer resistance than those prepared with PVDF binder. It implied that the kinetic process of lithium ion transfer may not be affected by the different binders [13], but the value of kinetic parameters could be impacted by changing the binder.

Towards a better understanding of the related interfacial impedance, the impedance data were fitted into an appropriate equivalent electrical circuit analysis using Zsimpwin software computer program as shown in Fig. 3 [23,24]. Based on the model fitting, it has the relatively smaller resistances of both the SEI and the charge transfer of lithium ion transport in the electrode prepared with SPEEK-FSA-Li binder (see Table 1). It reflects that the electrode prepared with SPEEK-FSA-Li binder may have a less resistance SEI film and a faster charge transfer than that prepared with PVDF binder. It can be attributed to the ionic conductivity of lithiated ionomer binders. The ionic conductivity for PC swollen SPEEK-FSA-Li membrane is close to $10^{-4} \text{ S cm}^{-1}$ at room temperature (conductivity of SPEEK-FSA-Li membrane in Supplementary information). Further research about the ion conductive SPEEK-FSA-Li membrane is going on.

3.3. Charge–discharge performance

Fig. 4A showed the charge–discharge curves of the LiFePO_4 electrode prepared with SPEEK-FSA-Li and PVDF binder at 0.5 C,

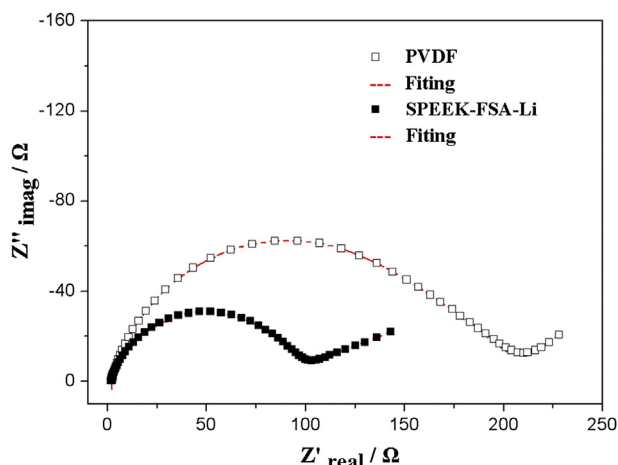
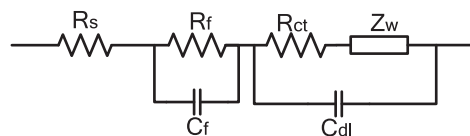


Fig. 2. Electrochemical impedance spectra of LiFePO_4 electrode prepared with SPEEK-FSA-Li or PVDF binder.



R_s : resistance of the liquid electrolyte
 R_f : resistance of solid electrolyte interphase (SEI)
 R_{ct} : resistance of charge transfer at the interface between SEI and LiFePO_4
 Z_w : Warburg impedance of lithium ions in LiFePO_4 electrode

Fig. 3. The equivalent circuit for the fitting of the experimental electrochemical impedance spectra of lithium ion intercalation or de-intercalation.

respectively. Both charge and discharge curves of two electrodes are almost in parallel with each other. Clearly, it was that the electrode prepared with SPEEK-FSA-Li binder showed better charge and discharge performances than that prepared with PVDF binder, including a lower charge plateau potential, a higher discharge plateau potential, and a larger discharge capacity. Specifically, the charge plateau potential is 3.49 V for the electrode prepared with SPEEK-FSA-Li binder, while it is 3.57 V for that prepared with PVDF binder. Meanwhile, the discharge plateau potential is 3.37 V for the electrode prepared with SPEEK-FSA-Li binder, which is about 0.08 V higher than 3.29 V for that prepared with PVDF binder.

Fig. 4B compares discharge capacity for cells with SPEEK-FSA-Li and PVDF as the cathode binder at 0.1 C, 0.5 C, 1 C and 2 C discharge rates. Prior to each discharge, all cells were charged to 4.2 V at the same rate as the discharge rate. As expected, specific capacity of both types of cathodes decrease at higher rates. In comparison, the electrode with ionic binder shows smaller decrease in capacity with the increasing of cycle rate. These results indicate that, for the electrode prepared with SPEEK-FSA-Li, the increase in the capacity and discharge plateau potential may come from faster charge transfer and the decrease in the polarization resistance, in agreement with the conjecture obtained from previous sections.

3.4. Adhesion characterization

The adhesion strength of the binder is an important factor for keeping contact between the coating and the current collector, and also between the electrode materials and carbon black [25]. To evaluate the adhesion strength between coating and the Al current collector, 180° peeling test was employed to measure the adhesion strength on a coated strip. As shown in Fig. 5, the adhesion of the electrode containing SPEEK-FSA-Li binders is much stronger than that containing the PVDF binder. The peeling strength of the LiFePO_4 /Super P/PVDF (8:1:1) electrode is 0.40 N and those of the electrodes prepared with SPEEK-FSA-Li binder are 2.13 N. The adhesion strength of electrode prepared with SPEEK-FSA-Li is more than five times greater than that with PVDF. Even when the content of SPEEK-FSA-Li binder is reduced to 5 wt %, the peeling strength is still 1.9 times as greater as PVDF binder with 10 wt%. This means that SPEEK-FSA-Li adhesive can firmly bond the coating on the current collector and thus endure repeated discharging–charging processes.

Table 1
Resistance values obtained from fitting impedance spectra.

Binder type	$R_s/\Omega \text{ cm}^{-2}$	$R_f/\Omega \text{ cm}^{-2}$	$R_{ct}/\Omega \text{ cm}^{-2}$
PVDF	2.13	43.76	147.70
SPEEK-FSA-Li	1.71	8.60	88.58

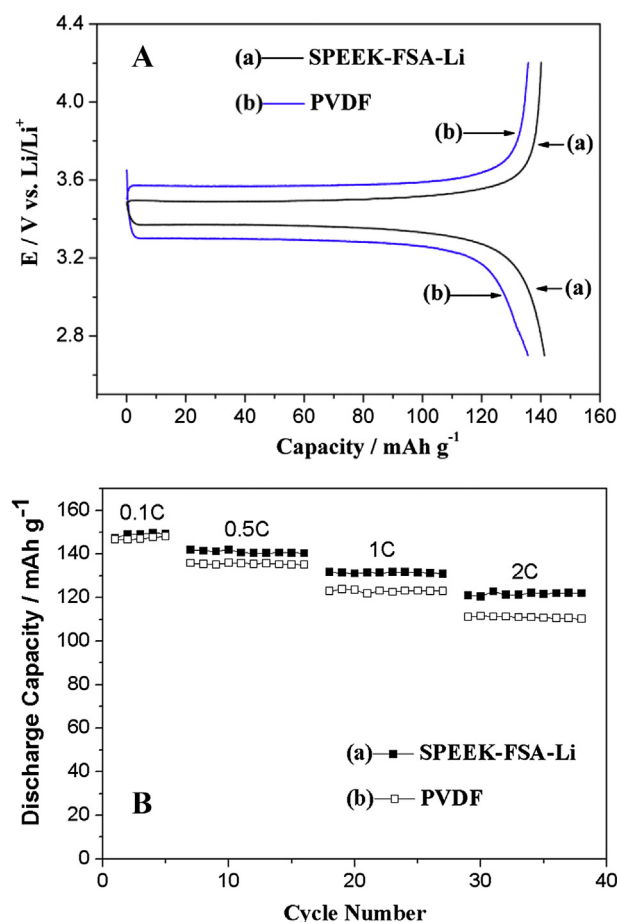


Fig. 4. (A) Charge–discharge voltage profiles and (B) rate performance of LiFePO₄ electrodes with SPEEK-FSA-Li ionic binder or PVDF at room temperature.

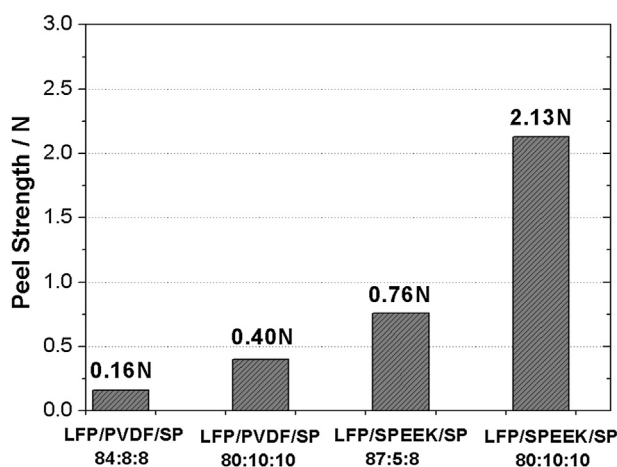


Fig. 5. Comparison of peeling strength of electrodes bound by different binders.

4. Conclusions

In this work, we report the study of ionomer binder based on SPEEK-FSA-Li, in which lithiated fluorinated sulfonic side chains

could enhance the ionic conductivity. The results have proved that the ionomer polymer has good electrochemical stability for cathode binder. EIS analysis illustrates that the electrode prepared with SPEEK-FSA-Li binder could benefit the formation of a less resistance SEI film and a faster charge transfer in the electrode. The ionic conductivity binder could compensate for the electrolyte depletion from the electrode porous space during cycling. Further, the improved charge–discharge plateau potential and discharge capacity of the electrode prepared with SPEEK-FSA-Li binder are thought to be due to the decrease in the polarization resistance. And SPEEK-FSA-Li binder exhibits excellent adhesion strength to ensure the stability of electrode. We believe that this study provides useful clues for design and elaboration of a new class of ionic conductivity binders that will further improve charge–discharge performance of lithium-ion batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.01.018>.

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